Numerical studies of the effects of process conditions on the development of the porous structure of adsorbents prepared by chemical activation of lignin with alkali hydroxides
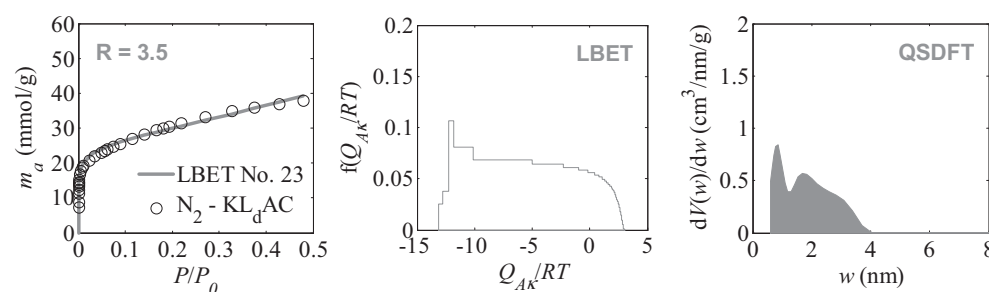
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GRAPHICAL ABSTRACT

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ABSTRACT

This paper presents the results of the application of the advanced LBET and QSDFT methods compared to the BET and DR approach to the comprehensive analysis of the porous structure of activated carbons obtained by chemical activation of demineralised Kraft lignin with potassium and sodium hydroxides. Based on the analysis of nitrogen adsorption isotherms, the influence of the preparation process conditions on the porous structure formation was investigated. Particularly, the impact of the type of activating agent, the activation temperature, the hydroxide to lignin mass ratio, and the flow rate of inert gas on the porous structure formation was assessed. This work proves how useful the used methods of structure analysis are when evaluating the influence of preparation conditions on the formation of the porous structure of activated carbons.

1. Introduction

Chemical activation using potassium hydroxide, KOH, or sodium hydroxide, NaOH, as the activating agent is an effective method for producing activated carbons [1–5]. This method proved to be highly advantageous with respect to physical activation with steam or carbon dioxide. Its major advantages are the greater efficiency of the process and the fact that it is carried out in one single stage involving lower temperatures and shorter durations, as well as a significantly enhanced development of the porous structure and the possibility of obtaining a porous structure with a limited range of pore widths. The disadvantages of chemical activation using alkali hydroxides include higher process costs than for physical activation, the requirement of adding a rinsing step, and considerable corrosion due to the use of hydroxides. But, interestingly, the development of the final porous structure

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can be altered to a considerable degree, depending on the conditions of chemical activation.

As a consequence, the choice of a suitable precursor is not less important than the selection of the adequate production technology and the determination of the optimum process conditions. Therefore, the search for new raw materials is still of interest, and particular attention is being paid in this regard to biomass waste from food and timber industries, and from agriculture. In addition to its physical, chemical and mechanical properties, the key arguments in favour of biomass waste include a relatively low cost and its general accessibility and renewability. From this point of view, plant wastes are very useful as raw materials for the production of activated carbons. Guo et al. [6] presented the results of activated carbons preparation from rice hulls by chemical activation with potassium and sodium hydroxides as activating agents. The research revealed that the materials obtained with KOH usually had surface areas exceeding 3000 m^2/g, while the surface area of those obtained with NaOH was around 2500 m^2/g. These results confirmed earlier conclusions from the same group, namely that porous carbons prepared by NaOH activation have larger average pore diameters than those derived from KOH activation. Additionally, KOH activation produces porous carbons with a higher micropore volume than in the case of NaOH [7].

One of the most promising materials for the production of activated carbons is lignin [8–12], being the second most abundant natural polymer in the world, surpassed only by cellulose. Out of all the polymers found in plant cell walls, lignin is the only one that is not composed of carbohydrate monomers. Lignin is based on up to three different phenyl-propane monomers, depending on the species. Coniferyl alcohol occurs in all species and is the dominant monomer in softwood. Deciduous wood species contain up to 40% syringyl alcohol units while grasses and agricultural crops may also contain coumaryl alcohol units. Concerning the preparation of activated carbons, lignin is particularly advantageous because of its high phenolic content, leading to higher carbon yields than those obtained from the two other main macromolecular compounds of biomass: cellulose and hemicellulose [11,12]. Hayashi et al. also presented interesting results dedicated to chemical activation of lignin with KOH, NaOH, ZnCl$_2$ and H$_3$PO$_4$ as activating agents, the weight ratio of the activator to the raw material being 1:1 [13]. From these results, the authors observed that ZnCl$_2$ and H$_3$PO$_4$ are effective activating agents at temperatures below 873 K, while KOH and NaOH are more efficient above 873 K [13].

However, generally speaking, optimising activation conditions through the choice of a suitable carbonaceous precursor and that of relevant activation parameters in order to meet given technological, economic and ecological specifications, is a huge experimental task. Many experiments are indeed required before the expected activated carbon designed for a particular adsorptive process is obtained, and a reliable analysis of the obtained results is necessary. However, the tools used for analysing the microporous structure of carbonaceous adsorbents, e.g. based on BET [15] and DR [16] theories, do not provide any information about the effect of the said preparation conditions on the formation of the microporous structure. This is partly because BET and DR methods are based on too many simplified assumptions, including the supposed homogeneity of the surface of each evaluated material, which can significantly decrease the credibility of the analyses' results. Apart from that, these methods provide few information on the structure of pores and the process of adsorption occurring in them. The information received with the use of the BET and DR methods is useful only in the case of comparative analyses, which are not enough when a precise technology and production conditions of activated carbons, designed for a specific use in advanced industrial processes, have to be chosen.

Consequently, the idea of the present work was, based on nitrogen adsorption isotherms, to carry out comprehensive analyses of the influence of the preparation process conditions on the porous structure formation of activated carbons obtained by chemical activation of demineralised Kraft lignin with potassium and sodium hydroxides.

2. Materials and methods

In our previous work, activated carbons were produced from demineralised Kraft lignin (KL$_d$) by chemical activation using two hydroxides, NaOH and KOH, as activating agents [14]. The lignin was supplied by Lignotech Iberica S.A (Spain), and underwent an additional process for removing the inorganic matter with the use of H$_2$SO$_4$. KOH and NaOH granules were ground and physically mixed with demineralised kraft lignin KL$_d$, according to various hydroxide/KL$_d$ mass ratios R, and next the hydroxide-lignin mixtures were subjected to heat-treatment in inert atmosphere [14]. The activation was carried out in a horizontal furnace flushed with nitrogen at various temperatures T (°C), hydroxide to raw material mass ratios R (dimensionless), activation times t (min), inert gas flow rates F (cm^3/min), and heating rates r (°C/min) [14].

At that moment, surface area and pore volumes of the activated carbons, here called, KL$_d$AC, were determined from the corresponding nitrogen adsorption isotherms obtained at −196 °C by using BET [15] and DR [16] simple methods, respectively. Herein two entirely different methods, LBET [17–22] and QSDFT [23–25], were applied to the nitrogen adsorption isotherms for describing the microporous structure of the KL$_d$AC adsorbents. Those methods of heterogeneous surface assessment of porous materials were especially applied to evaluate the impact of the type of activating agent, the activation temperature, the hydroxide to lignin mass ratio, and the flow rate of inert gas on the porous structure formation. The results of the performed analyses were also compared with the results obtained by means of the BET and DR methods. Such analyses also aimed at comparing and providing information on the usefulness of the used methods of analysis of the structure, i.e., the BET [15], DR [16], LBET [18–22] and QSDFT [23–25] methods, for evaluating of the influence of preparation conditions on the formation of the porous structure, as well as the consistency of the obtained information on the structure of pores and adsorptive properties of materials.

The LBET method was described in detail in former works [19–21]. It is based on the original models of adsorption on heterogeneous surfaces, originating from a unique multilayer adsorption theory, which introduced important generalisations of the BET model [18–22]. In this method, the original numerical fast multivariate identification of the adsorption systems procedure was implemented. The LBET method can be used for analysing the microporous structure of various carbon adsorbents, in which the micropores are a significant part of the overall porosity. The group of analytical models of LBET class is expressed using the following general form [18–22]:

$$\frac{m_a}{m_{hA}} = (1-\alpha)\left\{ 1 - \frac{1}{\ln(B_{A1}/B_{f1})} \cdot \ln\left(\frac{B_{A1}+\pi}{B_{f1}+\pi}\right) \right\}$$
$$+ d \cdot \alpha(1-\alpha)(1+\beta\theta_{22})\left\{ 1 - \frac{1}{\ln(B_{A2}/B_{f2})} \ln\left(\frac{B_{A2}(1-\theta_{22})^\beta + \pi}{B_{f2}(1-\theta_{22})^\beta + \pi}\right) \right\}$$
$$+ \alpha^{d+1}\left[d + (\beta\theta)^d\left(1 + \frac{\beta\theta}{1-\alpha\beta\theta}\right) \right]\left\{ 1 - \frac{1}{\ln(B_{A2+d}/B_{f\theta})} \ln\left(\frac{B_{A2+d}(1-\theta)^\beta + \pi}{B_{f\theta}(1-\theta)^\beta + \pi}\right) \right\}$$

(1)

where m_a is the amount of adsorbate (mmol/g), m_{hA} is the total number of primary sites (mmol/g) such that $m_{hA} = V_{hA}/V_p$, V_{hA} being the first adsorption layer capacity (cm^3/g) and V_p being the molar volume of adsorbate (cm^3/mmol), θ is a layer coverage ratio, π is